

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT SPECIFICATION

NO DRAWINGS

922,459



Date of Application and filing Complete Specification June 27, 1960.

No. 22486/60.

Application made in Germany (No. 28797 IVb/39c) on June 27, 1959.

(Patent of Addition to No. 922458 dated June 1, 1959).

Complete Specification Published April 3, 1963.

Index at acceptance:—Class 2(6), G1(B1:C1), G2B, G3(A2:C2:C3), G4A.

International Classification:—C08f.

COMPLETE SPECIFICATION

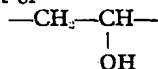
Process for the Manufacture of Modified Polyvinyl Alcohols

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of Frankfurt(M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a process for the manufacture of modified polyvinyl alcohols.

15 It has already been proposed to prepare water-soluble modified polyvinyl alcohols by subjecting a graft polymer prepared from one or more vinyl esters and, if desired, a compound copolymerisable with those vinyl esters, on a polyalkylene glycol, to complete or partial saponification or deesterification in an acid or alkaline medium.

20 The term "modified polyvinyl alcohols" was intended to mean those water-soluble polymeric compounds which consist of at least 50% by weight of

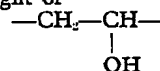


units.

30 The product so obtained in which the structure of the trunk polymer used as starting material is completely retained, possesses a series of valuable technological properties.

35 The present invention is based on the observation that valuable saponification or deesterification products of the above graft polymers which are soluble in cold water can also be obtained by graft-polymerising, in homogeneous phase, one or more vinyl esters on to one or more polyalkylene glycols or polyalkylene glycol derivatives under the influence of a free-radical forming polymerisation initiator and partially saponifying the resulting graft polymers so that the resulting novel modified polyvinyl alcohols contain at

most 50% by weight and preferably 20 to 49.9% by weight of



units.

The free radical polymerisation initiator may be present in an amount of from 0.01 to 10 per cent, calculated on the weight of the monomers.

50 The above products are predominantly obtained by partially saponifying or deesterifying those graft polymers which have been obtained by polymerising vinyl esters in the presence of a polyethylene glycol, or by saponifying or deesterifying those graft polymers which have been prepared in the presence of an oxyethylated polypropylene glycol or a higher homologue of polypropylene glycol.

60 The saponification or deesterification is carried out batchwise or continuously in a manner known as such in the presence of a solvent or a solvent mixture, for example methanol or methanol/water, if desired, in an inert gas atmosphere, for example under nitrogen.

70 When the saponification or deesterification is carried out in an alkaline medium, sodium hydroxide or potassium hydroxide, for example, which is dissolved in methanol is used as a catalyst. It is generally sufficient to add the alkali in a catalytic proportion. Saponification may be carried out at room temperature or at a higher temperature.

75 The degree of saponification desired can be predetermined in the usual manner firstly by varying the catalytic proportion of alkali added and secondly by interrupting the saponification reaction in the desired stage by adding a small proportion of an acid in order to neutralize the alkaline catalyst.

80 Alternatively, partially saponified products can be obtained by making use of the dif-

ferent rate at which the various copolymerized vinyl esters undergo saponification. For this purpose, for example, a graft copolymer of vinyl formate/vinyl stearate which has been prepared in the presence of polyalkylene glycol, is used as starting material.

Furthermore, the modified polyvinyl alcohols obtained by the process of this invention can be saponified or deesterified in an acid medium, for example in the presence of sulphuric acid, and the resulting saponification products, may, if desired, be partially acetalized in a simultaneous or subsequent operation.

The present invention is specifically directed to the manufacture of those modified polyvinyl alcohols which, due to their graft structure contain:—

- 1) Bound units of polyalkylene glycol and
- 2) Also contain incorporated hydrophobic organic groups, for example polyvinyl acetate groups, and more especially contain those two components in a proportion by weight such that the macromolecule contains less than 50% by weight of polyvinyl alcohol units which have been formed by saponification.

The modified polyvinyl alcohols obtained by this invention should contain the aforesaid polyvinyl alcohol units in a proportion such that the former are at least soluble in cold water, for example water at 10° C. (lower limit).

This requirement depends substantially on the type and quantity of polyalkylene glycol contained in the graft polymer used as starting material, and on the content of hydrophobic groups in the saponified product.

The presence of chemically bound polyalkylene glycol in the starting graft polymer makes it possible to obtain in the modified polyvinyl alcohol (which is obtained from said graft polymer by saponification or deesterification) an extremely great proportion of hydrophobic organic groups, without the modified polyvinyl alcohol losing its water-solubility.

It has unexpectedly been found that the water-solubility of the products obtained by this invention is not impaired by those hydrophobic groups but even considerably promoted. When, however, the proportion of those hydrophobic organic groups in the macromolecule exceeds a certain limit, turbidity phenomena are liable to occur on heating the aqueous solutions.

The graft polymers used as starting material in the process of this invention are preferably prepared by the process described in Application No. 12886/59 (Serial No. 922,457), by polymerizing in the homogeneous phase vinyl esters, such as vinyl propionate, vinyl butyrate, vinyl stearate, advantageously vinyl acetate, alone or in admixture with one another in the presence or absence of a further copolymerizable compound,

and in the presence of a polyethylene glycol or its derivatives, if desired with the use of a solvent. As polyethylene glycols there may be mentioned more especially water-soluble polyethylene glycols having a molecular weight of 10000 up to several millions. There may also be used water-soluble derivatives of those polyethylene glycols, for example a polyethylene glycol unilaterally or bilaterally esterified or etherified at its terminal hydroxylic groups, or more especially oxyethylated polypropylene glycols and corresponding homologues thereof. Still further, there may be used those derivatives in which one or both hydroxyl groups carry a monofunctional or polyfunctional amine or amide as substituent, and also water-soluble reaction products of those derivatives with monoisocyanates or polyisocyanates.

The amounts of polyethylene glycol or polyethylene glycol derivative originally contained in bound form in the starting graft polymer are completely retained in the saponification product.

The novel modified polyvinyl alcohols obtained by the process of this invention possess valuable technological properties. They can be used with particular advantage as surface-active and interfacially-active substances, for example as protective colloid for the dispersion polymerization, as starting material for making foamed substances, such as sponges etc.

The novel modified polyvinyl alcohols can also advantageously be used for making soft, readily water-soluble and well-transparent films that can be processed from their solutions or in the thermoplastic state.

Still further, the products obtained by this invention can be used as textile auxiliary agents, sizing and finishing agents, and for cosmetic purposes.

The following examples illustrate the invention, the parts being by weight unless otherwise stated.

EXAMPLE 1

Preparation of the graft polymer used as starting material.

In a glass flask provided with a reflux condenser and a dropping funnel 5—10 parts of a solution consisting of:—

160 parts vinyl acetate
40 parts polyethylene glycol (molecular weight: 25000)

4 parts dibenzoyl peroxide
were slightly polymerized by being heated at 80° C. on the water bath.

After the polymerization had set in, the residual portion of the solution was added dropwise within about 2 hours. After the polymerization mixture had been added, the bath temperature was raised within 1—2 hours to 90° C. to complete the polymerization, whereby the reflux came to a standstill. Unreacted monomer was then removed at that

70

75

80

85

90

95

100

105

110

115

120

125

130

temperature by means of a pulsating vacuum.

A clear, colourless graft polymer having a K-value of 45 (1% solution in ethyl acetate) (Fikentscher, *Cellulosechemie*, vol. 13, page 58 (1932) was obtained in a yield of 198 parts.

Partial saponification or deesterification:—
350 parts of the above graft polymer were dissolved in 641 parts methanol and 9 parts water, and 37 parts of a methanolic sodium hydroxide solution of 5% strength by weight were stirred at 25° C. into the solution obtained.

The resulting mixture was stirred for about 1 hour at 30° C. until it commenced to thicken. Stirring was interrupted and the gel which had formed was maintained at 30° C. for 4 hours.

Subsequently, pure steam was blown into the gel obtained, the whole was stirred and distilled with steam until all organic solvent had been expelled from the reaction vessel and an aqueous solution of about 25% strength by weight of the saponification product had formed.

The saponification product was composed as follows:—

	By weight
Polyvinyl acetate units in the macromolecule - - - -	25%
Polyvinyl alcohol units in the macromolecule - - - -	4%
Polyethylene glycol units in the macromolecule - - - -	32%

EXAMPLE 2

A graft polymer was prepared in the manner described in Example 1 from:—

50 parts vinyl acetate
49 parts oxyethylated propylene oxide having the following characteristic data:—
Molecular weight: about 5000
OH-number/23
Oxyethyl content: about 70%
Molecular weight of polypropylene oxide used: 2000

1 part dibenzoyl peroxide.
The graft polymer was purified by heating a 10% aqueous solution to about 70° C., separating the precipitated product, washing it with hot water and drying it *in vacuo* at room temperature.

Saponification or deesterification:—

100 parts of the above product were dissolved in 180 parts methanol, and 2.6 parts water and subsequently 12 parts methanolic sodium hydroxide solution of 5% strength were added. The resulting reaction mixture was stirred for 5 hours at 30° C. After 1 hour, a viscous phase was obtained which, however, was not so viscous that stirring had to be interrupted. On cooling to room temperature, a gel was obtained into which pure water vapour was introduced. The methanol/methyl acetate was distilled off and a clear

aqueous solution was obtained. The product was isolated from the aqueous solution by evaporating it and dried *in vacuo* at 40° C. until its weight was constant.

The product obtained contained vinyl alcohol groups in the macromolecule in a proportion of 27.3% by weight.

EXAMPLE 3

Preparation of the graft polymer used as starting material.

In a vessel provided with a stirrer and a reflux condenser 300 parts polyethylene glycol (molecular weight about 25000) were melted at 90° C. water bath temperature, and 50—100 parts of a solution of:—

1700 parts vinyl acetate and
16 parts dibenzyl peroxide
were then introduced into the melt obtained. Polymerization set in after a short time and the residual portion of the above solution was added dropwise within 1 hour with continuous slow agitation.

5 minutes after all monomer had been added, 600 parts methanol were slowly dropped into the reaction mixture. The ventilating opening of the reaction vessel was closed and a pressure of 1.5—2.5 atmospheres absolute was produced in the vessel by means of nitrogen. Polymerization was then gradually completed within 6 hours and with slow agitation under that pressure and at a water bath temperature of 80—90° C. After cooling and ventilation, the polymer solution obtained was diluted with 2000 parts methanol.

The solid content of that solution was diluted with methanol and adjusted to exactly 40% by weight.

Partial saponification or deesterification:—
478 parts of the above 40% polymer solution were mixed at 20° C. while stirring in a stirring vessel provided with a reflux condenser which could also be used for distillation, with 5.92 parts of a 14.45% solution of sodium hydroxide in methanol. After about 40 minutes, a "gel phase" was obtained, that is the saponification product formed had become insoluble in methanol and formed a temporarily viscous gel. 23 minutes after the formation of that "gel phase", a solution of 1.5 parts acetic acid in 35 parts methanol was stirred into the reaction product which meanwhile had become crumbly.

After 15 minutes, the condenser was commutated to distillation and the solvent was removed while stirring under a pressure of 40 mm mercury at 50° C. water bath temperature.

120 parts of a colourless, fine-powdered modified polyvinyl alcohol were obtained of which the macromolecules had the following average composition:—

27% vinyl acetate units
47% vinyl alcohol units
26% ethylene glycol units

EXAMPLE 4

The graft polymer used as starting material was prepared as follows:—

In a vessel heatable by means of a water bath and provided with a stirrer, a reflux condenser, a thermometer and a nitrogen inlet, 150 parts polyethylene glycol the terminal hydroxyl groups of which had been reacted with diisocyanate and which had a molecular weight of about 50000, were melted under a nitrogen atmosphere. The resulting melt was gradually mixed at 90° C. bath temperature and while stirring with a solution of 850 parts vinyl acetate, 8 parts dibenzoyl peroxide and 250 parts methanol. The reaction mixture was then polymerized for 6 hours at 95° C. bath temperature and under a nitrogen atmosphere of 1.5 atmospheres gauge.

The batch was then diluted with methanol to a solid content of 40%.

Saponification or deesterification:—

1000 parts of the methanolic graft polymer solution of 40% strength by weight prepared in the manner described above, were introduced into a vessel provided with a thermometer and a stirring means, and 10 parts water and 13.4 parts of a 15% by weight solution of sodium hydroxide in methanol were added at 20° C. while stirring. After about 30 minutes, the viscosity of the mass commenced to increase considerably and stirring was interrupted. The reaction was continued at 20° C. for 4 hours. The saponification was interrupted by adding 3.5 parts glacial acetic bath dissolved in 110 parts methanol.

The batch was subsequently dried *in vacuo* at 80° C., the modified polyvinyl alcohol being obtained in powder form. Analytical investigation indicated the following composition of the reaction product:—

Polyvinyl acetate units	-	-	27%
Polyvinyl alcohol units	-	-	48%
Polyethylene glycol units	-	-	25%

EXAMPLE 5

In the apparatus used in Example 4 and by the method described in that example a graft polymer solution was prepared from 620 parts polyethylene glycol (molecular weight: 25000)

1380 parts vinyl acetate
14 parts dibenzoyl peroxide
138 parts methanol.

Saponification or deesterification:—

The solution of graft polymer prepared in the manner described above was diluted in the same reaction vessel with 862 parts methanol and mixed at 20° C. while stirring with 91 parts of a 15% methanolic sodium hydroxide solution.

The reaction was complete after 4 hours. The reaction mixture obtained was subjected to steam distillation during which the methanol/methyl acetate mixture formed was

distilled off, and an aqueous solution of the modified polyvinyl alcohol was obtained. The modified polyvinyl alcohol so obtained was composed as follows:—

Polyvinyl alcohol units	-	-	44%
Polyvinyl acetate units	-	-	8%
Polyethylene glycol units	-	-	48%

EXAMPLE 6

Graft polymers:—

In the apparatus described in Example 4 and by the method described in that example a solution of a graft polymer was prepared from

820 parts polyethylene oxide (molecular weight: 4000)

1180 parts vinyl acetate and
12 parts dibenzoyl peroxide.

Saponification or deesterification:—

In the same reaction vessel in which the graft polymer was prepared, the molten graft polymer was dissolved in 3700 parts methanol and deesterified by adding 78 parts of a methanolic sodium hydroxide solution. Deesterification was complete in 5 hours. The resulting reaction product was processed in the manner described in Example 5. The modified polyvinyl alcohol was composed as follows:—

Polyvinyl alcohol units	-	-	35.7%
Polyvinyl acetate units	-	-	0.9%
Polyethylene glycol units	-	-	63.4%

EXAMPLE 7

The graft polymer solution described in Example 5 was used as starting material.

Saponification or deesterification:—

1000 parts of the graft polymer solution were diluted with 1692 parts methanol, and the resulting solution was mixed with 30 parts of a 78% sulphuric acid dissolved in 30 parts methanol.

The reaction was carried out at a water bath temperature of 58° C. while stirring continuously and was complete after about 15 hours.

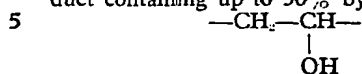
The sulphuric acid was then neutralized with a methanolic sodium hydroxide solution, steam was introduced into the reaction mixture, a methanol methyl acetate mixture was distilled off, and an aqueous solution of a modified polyvinyl alcohol was obtained. The modified polyvinyl alcohol so obtained was composed as follows:—

Polyvinyl alcohol units	-	-	46.3%
Polyvinyl acetate units	-	-	2.8%
Polyethylene glycol units	-	-	50.9%

WHAT WE CLAIM IS:—

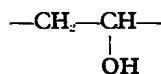
1. A process for the manufacture of a modified polyvinyl alcohol soluble in cold water, which comprises graft-polymerising, in homogeneous phase, one or more vinyl esters onto one or more polyalkylene glycols or polyalkylene glycol derivatives under the influ-

ence of a free radical-forming polymerisation initiator, and partially saponifying the resulting graft polymer so that a water-soluble product containing up to 50% by weight of



units is obtained.

2. A process as claimed in Claim 1, wherein the graft polymer is partially saponified to such an extent that a product soluble in cold water containing from 20 to 49.9% by weight of



units is obtained.

3. A process as claimed in Claim 1 or 2, wherein a mixture of a vinyl ester and a compound copolymerizable with it is graft-polymerized on to one or more polyalkylene glycols or polyalkylene glycol derivatives.

4. A process as claimed in any one of Claims 1—3 wherein vinyl acetate is used as the vinyl ester. 20

5. A process as claimed in any one of Claims 1—4, wherein a polyethylene glycol is used as the polyalkylene glycol.

6. A process as claimed in any one of Claims 1 to 5, wherein the free radical polymerisation initiator is present in an amount of from 0.01 to 10 per cent, calculated on the weight of the monomers. 25

7. A process for the manufacture of a modified polyvinyl alcohol soluble in cold water as claimed in Claim 1 and conducted substantially as described in any one of the examples herein. 30

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.